the bonding and antibonding levels of the decaborane framework. There are four such nonbonding orbitals on the two iodine atoms with C_{2v} symmetry b_1, a_2, b_2, and a_1. These four orbitals mix to varying extent with framework orbitals with the strongest mixing between the iodine p_x orbitals and the "linear three-center orbital" connecting Atoms 5, 2, 7 on one end and Atoms 8, 4, 10 on the other in the simple ECL description.[3]

The transition may then be described as an allowed transition, polarized in the x direction, in which an electron originates in an orbital which is a combination of an iodine nonbonding orbital and a localized three-center framework orbital, and terminates on the same nonbonding orbital of the boron framework responsible for the transition in decaborane. Thus, the transition has many similarities to the $n\rightarrow\pi^*$ transitions encountered in benzene derivatives. This qualitative description also accounts for a shift of charge from the iodines into the framework with a consequent decrease of the dipole moment of the excited state relative to that of the ground state as implied by the solvent shifts observed.

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On the Theory of Shifts and Broadening of Electronic Spectra of Polar Solutes in Polar Media*

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When a polar-solute molecule undergoes an electronic transition and forms a state of different polarity, the Franck–Condon principle shows that the new system is first formed in a nonequilibrium thermodynamic state. An expression for the spectral shift and broadening by a series of solvents of differing polarity is derived in the present paper in terms of thermodynamic properties of certain equilibrium distribution systems. For this purpose use is made of a recent particle description of nonequilibrium and equilibrium polar media, which emphasizes functional dependence and avoids, thereby, the usual more specific assumptions. A relation between the broadening and the shift is then deduced under certain conditions. Expressions are also derived for the effect of pressure and temperature on the shift, in terms of the polar contribution to the volume and entropy of solvation, respectively, and for the influence of applied electrical fields. An expression is obtained for the solvent-reversal shift of Brooker in terms of the polarizability difference of the initial and final states of the solute. Introduction of more specific assumptions is then made for purposes of comparison with earlier works, which constitute special cases of the present one, and for estimation of dipole moments and polarizabilities of excited states from spectral and electrical shifts.

INTRODUCTION AND OUTLINE OF PAPER

WHEN a polar molecule in a polar medium absorbs or emits light to form a relatively nonpolar electronic state, a large spectral shift occurs, the shift being a blue one in absorption and a red one if a polar solute fluoresces (see Refs., e.g., 1–5). When the initial state of the solute is polar and the solvent medium is polar the observed spectral shifts are large—of an order of magnitude greater than the usual red shifts due to dispersion forces.

Theoretical treatments for the polar contribution to the spectral shift are few in number.[1–3] They have employed second-order quantum-mechanical perturbation theory for computing the potential energy in the initial and final state. A thermodynamic average of this energy difference (an average over the initial state because of the Franck–Condon principle) has been estimated by evaluating various contributions with the aid of a permanent dipole–induced-dipole model for the polar part of the interactions. The dipolar solute was regarded as being embedded on a dielectric continuum.[1–3] In these perturbation treatments polar

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[1] Y. Ooshika, J. Phys. Soc. Japan **9,** 594 (1954).

[2] (a) E. Lippert, Z. Naturforsch. **10a,** 541 (1955); Z. Physik. Chem. (Frankfurt) **6,** 125 (1956); (b) E. Lippert, Z. Elektrochem. **61,** 962 (1957); (c) compare N. Mataga, Y. Kaifu, and M. Koizumi, Bull. Chem. Soc. Japan **28,** 690 (1955); **29,** 465 (1956).

[3] (a) E. G. McRae, J. Phys. Chem. **61,** 562 (1957); (b) Spectrochim. Acta **12,** 192 (1958).

[4] K. Dimroth, C. Reichardt, T. Siepmann, and F. Bohlmann, Ann. Chem. **661,** 1 (1963). This article also contains extensive references to recent experimental work on spectral shifts.

[5] S. F. Mason, Quart. Rev. (London) **15,** 287 (1961).

and second-order dispersion contributions to the spectral shift were additive.[6]

With the aid of a recently developed formalism[7,8] for treating polar media under equilibrium and nonequilibrium conditions the above work can be both generalized and simplified in certain respects, and other properties such as the polar contribution to broadening can be calculated. The formalism employs second-order perturbation theory for solute–medium interactions, as before, but makes no such assumption for interactions within the medium and it employs no specific model for the solute (e.g., no permanent and induced point dipole in a sphere, imbedded in a continuum). The formalism describes instead the functional dependence of the solute–medium interactions on the permanent and induced charge distributions. One can then introduce into the final expressions typical specific models used in the literature for computing polar interactions, since they are automatically included as special cases, and compare with and extend earlier work. Certain relationships are deduced later independently of such models, however.

Equations (13), (24), and (29) are obtained for the polar contribution to the spectral shift and to broadening. Formal expressions are obtained from (13) and (29) for the effect of pressure, of temperature ("thermochromism"), and of external electric fields ("electrochromism") on the shift. Under a certain condition ("orthogonal" initial and final charge distributions, as defined later) the broadening and the spectral shift are predicted here to be simply related. Some comparison with the data is given. A specific example of the above "orthogonality" occurs if one of the two states of the solute is nonpolar. An independent test for such nonpolarity can be made by measuring solvent effects on both absorption and fluorescence spectra.

Under the "orthogonality" condition, it is shown, the spectral shifts in various polar solvents should bear a simple relation to the polar contribution to solvation free energies: Differences in spectral shifts in various polar solvents are calculated to equal twice the differences in the polar contribution to the solvation free energy. The factor of 2 arises because of "orientation strain" in the final state. Under such conditions at least, and perhaps more generally, one would then expect some parallelism of spectral shifts of different solutes in a series of solvents. Such a parallelism has been found in a number of studies[2,4,9,10] though there are occasionally highly specific effects. A related parallelism with effects of different polar solvents on the free energy of activation of a reaction involving a polar transition state has also been found.[9b] A numerical estimate of the polar contribution to the free energy of solvation of some dipolar solutes is made in the present paper from the spectral data.

For purposes of comparison of Eq. (13) for the spectral shift with previous equations in the literature, the particular form which this equation takes when the medium is treated as a dielectric continuum and when the solute is treated as a dipole in a sphere is also considered. Extension of the equations to ellipsoidal shapes (from spherical ones) and to separated charge distributions (from point-dipole ones) is also given.

The separated-charge model reveals that the point-dipole approximation yields too high a result for dipole moments estimated from spectral shifts, though the error is negligible when the charge separation is small enough (e.g., the ion-pair pyridinium iodide[9a] mentioned in Appendix II). To correct for this effect, Lippert adjusted the radius of the sphere to some effective radius,[2b] using a correction factor estimated from a comparison of solvation free energies for the point-dipole and separated-charge spherical model of a zero-polarizable solute. One can now use instead an expression for the shift directly, derived for any given model. Lippert also considered a point-dipole zero-polarizability ellipsoidal model.[2b]

The dipole moment of excited states calculated from spectral-shift formulas may be compared[10] with those obtained from measurements of electrical dichroism and of fluorescence polarization in electric fields. They are comparable, but those calculated from spectral shifts are slightly too large, suggesting that the extent of charge separation is slightly larger than previously estimated. Dipole moments of charge-transfer complexes have also been estimated by each method.[10]

In the case of some merocyanines there is a peculiar reversal of spectral shift with solvent polarity, beyond a certain polarity.[3b,11] This shift has been interpreted in two ways that are qualitatively not dissimilar.[3b,11]

[6] London dispersion forces (induced-dipole–induced-dipole) are second order and have an approximately $1/R^6$ potential-energy function. An estimate of their contribution to spectral shifts has been made, for example, by H. C. Longuet-Higgins and J. A. Pople [J. Chem. Phys. **27**, 192 (1957)], and the dispersion terms also occur in the work of Ooshika[1] and of McRae[3]. Coupling between the dispersion forces and "polar" forces would then be expected to arise in higher-order terms. London dispersion force and polar contributions to the spectral shift are, one may conclude, additive within this approximation of second-order perturbation theory. To be sure, first-order dispersion forces, with an approximately $1/R^3$ potential-energy function, can occur between like species if at least one of them is excited to an optically allowed state (excitation-transfer forces). See, for example, R. S. Mulliken, Phys. Rev. **120**, 1674 (1960) and references cited therein.

[7] (a) R. A. Marcus, J. Chem. Phys. **38**, 1335 (1963); (b) compare **39**, 460 (1963).

[8] (a) R. A. Marcus, J. Chem. Phys. **39**, 1734 (1963); (b) compare **38**, 1858 (1963). A typographical error occurs in Eq. (13) of Ref. 8(a): The ½'s should be deleted. No equations deduced from (13) need correction.

[9] (a) E. M. Kosower, J. Am. Chem. Soc. **80**, 3253, 3261, 3267 (1958); *Molecular Biochemistry* (McGraw-Hill Book Company, Inc., New York, 1962), and references cited therein; (b) in Ref. 9(a) Kosower has compared these spectral shifts with Winstein's Y function, for example.

[10] J. Czekalla, Z. Elektrochem. **64**, 1221 (1960); Chimia **15**, 26 (1961); J. Czekalla and G. Wick, Z. Elektrochem. **65**, 727 (1961); J. Czekalla and K. O. Mayer, Z. Physik. Chem. (Frankfurt) **27**, 185 (1961); W. Liptay and J. Czekalla, Z. Naturforsch. **15a**, 1072 (1960).

[11] L. G. S. Brooker, G. H. Keyes, R. H. Sprague, R. H. Van Dyke, E. Van Lare, G. Van Zandt, F. L. White, H. W. J. Cressman, and S. G. Dent, J. Am. Chem. Soc. **73**, 5332 (1951); L. G. S. Brooker, G. H. Keyes, and D. W. Heseltine, *ibid.*, p. 5350.

The calculation for one of these interpretations[3b] is discussed and corrected. Independent knowledge or computation of the polarizability difference of ground and excited state would be extremely helpful here for testing any such model.

An application of the statistical-mechanical results is made to thermochromism.[12] It is concluded that under the "orthogonality" condition mentioned above the differences in the temperature coefficient of the position of the spectral maximum (in units of calories per mole per degree) for various solvents is twice the difference in polar contribution to the entropy of solvation of the solute for these solvents, but only when the nonpolar terms cancel. This polar contribution is then estimated from the spectral data of diphenyl betaine, a molecule with some appreciable separation of charge.

An application is also made to pressure effects on spectral shifts[13] and to the influence of external electric fields.[14] An expression is obtained for the polar contribution to the volume of solvation in terms of the pressure effect when the cited conditions are fulfilled, and as a particular case the magnitude of the pressure effect is predicted from the temperature effect under certain conditions. The electrical effect is expressed in terms of the dipole moments and polarizabilities of the two electronic states of the solute involved in the absorption or fluorescence, and may therefore provide information about them in favorable instances.

CONFIGURATIONAL POTENTIAL ENERGY AND SPECTRAL SHIFT

We use a recent "particle" description[7,8] for polar media. In the particle description the macroscopic system may be considered as composed of particles, each of which represents a single molecule or a whole collection of molecules. As one particle, one may select any "central species" s, whose behavior is of particular interest in the phenomenon under investigation, a solute molecule, for example. There may be one or more of these s in some phenomena (e.g., in bimolecular reactions). The remainder of the system, M, the "medium," can be treated as another particle. The symbol i is used to denote s or M when the remarks below apply to either.

At any given intraparticle configuration, each Particle i has a charge density at any point $\mathbf{r}$, $\rho_i^\circ(\mathbf{r})$. It is the sum of $\rho_i^\circ(\mathbf{r})$, its value at the same *intraparticle* configuration when i is isolated from all other particles, and of $\rho_i^{\text{in}}(\mathbf{r})$, the charge induced by the remaining particles at the given interparticle configuration. Both ρ_i° and ρ_i^{in} vary with $\mathbf{r}$ and both depend on the intraparticle coordinates; ρ_i^{in} depends on the interparticle ones as well. The potential at $\mathbf{r}'$ due to all particles but i, $\phi_i(\mathbf{r}')$, is given by (1)[7a]

$$\phi_i(\mathbf{r}')=\sum_{j\neq i}\int r^{-1}[\rho_j^\circ(\mathbf{r})+\rho_j^{\text{in}}(\mathbf{r})]d\mathbf{r}, \qquad (1)$$

where $r=|\mathbf{r}-\mathbf{r}'|$. The induced charge density in Particle j is related to this potential by means of a certain operator A_j, which has a symmetry property given by Eq. (35) of Ref. 7(a)

$$\rho_j^{\text{in}}(\mathbf{r})=A_j(\mathbf{r},\mathbf{r}'')\phi_j(\mathbf{r}''). \qquad (2)$$

Such a formulation has been shown to include the usual special cases employed in the literature to treat polar interactions in condensed phases,[7] and to include electrode systems as well as homogeneous ones.

The polar contribution to the interparticle potential energy of any configuration of the system is given by Eq. (3)[7]

$$U^{\text{pol}}=\tfrac{1}{2}\sum_i\int\phi_i\rho_i^\circ d\mathbf{r}. \qquad (3)$$

For any given interparticle and intraparticle configuration the remaining contribution to the total potential energy of the system, U, will be the sum of an interparticle nonpolar term, an intraparticle term for the medium when it is isolated at the given intraparticle configuration, and an intraparticle term for the central species when they are isolated at the given intraparticle configurations.[15] Expressions for the various symbols in the above equations in terms of electronic wavefunctions and their properties may be found in Ref. 7(a), but are not needed for derivation of the final equations, (13), (24), and (29).

For certain calculations, such as those of the spectral properties, it is convenient to consider the central species s at any specified nuclear configuration and to investigate their interaction with each other and with the remainder of the system, M. The many coordinates of M, τ, are allowed to fluctuate in accordance with the appropriate statistical-mechanical distribution. Classical statistical mechanics is used for this solvent motion, partly because of convenience and partly because much of the discussion is associated with orientational and translational motions. Some of the results should persist when a quantum distribution function is used, however, since the functional dependence of the distribution function on charge distributions is of major importance in the derivation, rather than the specific form of the distribution function.

The polar interparticle interactions influence the free energy of the system. We consider a system of any given volume. The polar contribution to its Helm-

[12] Experimental data on thermochromism have been reported by K. Dimroth, C. Reichardt, and A. Schweig, Ann. Chem. **669**, 95 (1963).

[13] Pressure effects on emission spectra of several organic compounds have been made by D. W. Gregg and H. G. Drickamer, J. Chem. Phys. **35**, 1780 (1961). However, there appear to be no measurements on polar compounds in polar media for which polar spectral shifts have been studied.

[14] Electrochromism for nonpolar systems has been studied by J. Kumamoto, J. C. Powers, Jr., and W. R. Heller, J. Chem. Phys. **36**, 2893 (1962).

[15] The "nonpolar" interparticle term includes London dispersion and electron exchange contributions to interparticle interaction, and is taken to be additive with the polar one. [6,7]

holtz free energy[16] at this constrained volume is defined as this Helmholtz free energy minus that of the uncharged system ($\rho_s^\circ=0$) for the same volume, and is denoted by F. Later in the derivation F is related to the Gibbs and Helmholtz free energies of charged and uncharged systems, each having an equilibrium volume appropriate to prevailing pressure p, thereby taking into account electrostrictive effects.

If $U(0)$ denotes U when all ρ_s° vanish, then F is given by Eq. (4)[8]:

$$F=-kT\ln\int\exp\left(\frac{-U}{kT}\right)d\tau\Big/\int\exp\left(\frac{-U(0)}{kT}\right)d\tau. \quad (4)$$

The values of $\rho_M^\circ(\mathbf{r})$ and of $\rho_i^{\text{in}}(\mathbf{r})$ at any point $\mathbf{r}$ depend not only on $\mathbf{r}$ but also on the coordinates of the instantaneous intraparticle configuration of the medium τ.

We also define a hypothetical "optical polarization" system as a system having a polar contribution to the free energy F^{op} given by (5)[8]

$$F^{\text{op}}=\langle U-U(0)\rangle, \quad (5)$$

where the average is with respect to the distribution function of the uncharged system

$$\exp\left(\frac{-U(0)}{kT}\right)\Big/\int\exp\left(\frac{-U(0)}{kT}\right)d\tau.$$

Thereby, the solvent medium in the [op] system responds to a charging of the solute molecule only via an electronic polarization of the solvent molecules.

For any configuration τ the potential-energy difference between the initial state [0] and the final state [1] of the system after light absorption or fluorescence, becomes the difference between "polar" and other terms, denoted by U^{pol} and U^{np}, respectively,

$$U_1-U_0=(U_1^{\text{pol}}+U_1^{\text{np}})-(U_0^{\text{pol}}+U_0^{\text{np}}). \quad (6)$$

By the Franck–Condon principle, U_1 and U_0 are to be evaluated at the same nuclear coordinates of the entire system, those of the initial state. The mean polar contribution to the spectral shift is $U_1^{\text{pol}}-U_0^{\text{pol}}$ averaged over the equilibrium configurational distribution function for this initial state of the entire system, at the given volume of the system. The volume of the system has no time to change during the rapid spectral transition. In the case of fluorescence we confine our attention to systems of solute molecules whose fluorescent lifetime is sufficiently long that most of them find themselves in an equilibrated solvent environment before fluorescing.

When saturation of electronic polarization is absent, we may expand U in powers of the ρ_s°, and, in this standard approximation, neglect powers higher than the second in all ρ_i°

$$U=U(0)+U(1)+U(2). \quad (7)$$

$U(0)$ is the sum of a term independent of ρ_i° and of one containing only the second power of ρ_M°[7a] $U(0)$ does not depend on ρ_s°. $U(1)$ is bilinear. It contains terms of the first power in ρ_s° and of the first power in ρ_M° and vanishes when either ρ_s° or ρ_M° vanishes. $U(2)$ contains terms of the second power in ρ_s° and is independent of ρ_M°.

Since the polar contribution to $U(0)$ is the same in the initial and final states, the polar contribution to the spectral shift, averaged over all configurations of the initial state [0], is given by (8), and is denoted by ΔE_T

$$\Delta E_T=\langle U_1^{\text{pol}}-U_0^{\text{pol}}\rangle_0$$
$$=\langle U_1(1)+U_1(2)-U_0(1)-U_0(2)\rangle_0, \quad (8)$$

where $\langle\ \rangle_0$ denotes the average with respect to the configurational distribution in the initial state [0] at the given volume

$$\langle f\rangle_0=\int f\exp\left(\frac{-U_0}{kT}\right)d\tau\Big/\int\exp\left(\frac{-U_0}{kT}\right)d\tau. \quad (9)$$

Equation (8) represents the shift for any given internal coordinates of the solute. One must then average over these vibrational coordinates, in accordance with the initial equilibrium distribution. If one neglects any dependence of the polar term (8) on the vibrational state, as we do, Eq. (8) then represents the polar shift.

FLUCTUATIONS

The deviation of any function y from its mean value $\langle y\rangle$ is denoted by δy,

$$\delta y=y-\langle y\rangle. \quad (10)$$

We neglect any correlations in the fluctuations of the polar and the nonpolar contributions to U_1-U_0.[17] That is, $\langle\delta(U_1^{\text{pol}}-U_0^{\text{pol}})\delta(U_1^{\text{np}}-U_0^{\text{np}})\rangle$ is assumed to vanish. For any spatial configuration of the atoms in the solute molecule, the fluctuations in the polar term are primarily due to rotational motions of the

[16] The Helmholtz free energy of a system in thermal equilibrium at temperature T, of arbitrary volume V, having the specified solute molecule at a specified intramolecular configuration of the solute and fixed in position, is $-kT\ln\int\exp(-H/kT)d\Omega/N!$. The $N!$ allows for indistinguishability of the solvent molecules, H is the Hamiltonian, $d\Omega$ is the phase-space volume element in γ space divided by the appropriate power of h, and the many-dimensional integration over $d\Omega$ is such that the system is confined to a volume V. (The $N!$ is replaced by a product of factorials if there is more than one "solvent" component, such as added salt or mixed solvents.) Integration over the momenta coordinates is straightforward, yielding the usual factor which is the same for the charged and uncharged systems and yielding a configurational integral $\int\exp(-U/kT)d\tau/N!$ The common factors cancel when the F's in Eqs. (4) and (5) are computed.

[17] Thereby, only the correlation of fluctuations in $U_1(1)+U_1(2)-U_0(1)-U_0(2)$ with fluctuations in the nonpolar contribution to U_1-U_0 is neglected. [Any polar term in $U_0(0)$ and $U_1(0)$ cancels in U_1-U_0.]

solvent molecules. The fluctuations in the nonpolar term are due at least in part to translational fluctuations of positions of the solvent molecules. There are also fluctuations in vibrational coordinates of the solute, and we ignore any correlations between this vibrational contribution to broadening and the polar contribution.

We obtain

$$\langle[\delta(U_1-U_0)]^2\rangle_0=\langle[\delta(U_1^{\rm pol}-U_0^{\rm pol})]^2\rangle_0 + \langle[\delta(U_1^{\rm np}-U_0^{\rm np})]^2\rangle_0. \quad (11)$$

We wish to calculate the polar term in (11). We first note that since $U(2)$ does not depend on ρ_M°, unlike $U(0)$ and $U(1)$, it is insensitive to the usual rotational and translational fluctuations of the medium that occur in condensed phases. Hence, we may neglect the $\delta U(2)$'s. From (7) and (11) we then obtain (12) for the polar contribution, δ^2, to the mean-square fluctuation in energy difference of the initial and final states

$$\delta^2=\langle[\delta(U_1^{\rm pol}-U^{\rm pol})]^2\rangle_0=\langle\{\delta[(U_1(1)-U_0(1)]\}^2\rangle_0. \quad (12)$$

EQUATIONS FOR THE SPECTRAL SHIFTS

The terms in (8) have been expressed in Ref. 8 in terms of certain free-energy changes. One can find the following result for the polar contribution to the spectral shift from Eqs. (15) and (18) of Ref. 8(a), applicable when the generalized polarizability operator A_s is the same in the two electronic states of the solute (a correction term for a change of A_s is given later):

$$\Delta E_T=F_1-F_0+F_{1-0}^{\rm op}-F_{1-0}. \quad (13)$$

In (13) F_1 and F_0 are the polar contributions to the Helmholtz free energy of a system in which the solute is in its final and initial electronic states, respectively, and in which the environment is in thermal equilibrium, but at the given initial volume V. F_{1-0} is the corresponding contribution for a hypothetical solute whose permanent charge distribution is that for the state [1] minus that for the state [0]. $F^{\rm op}{}_{1-0}$ is the polar contribution to the free energy of a system in which the medium responds to the [1]−[0] charge distribution only via an optical (i.e., electronic) polarization. These equations apply to dielectrically unsaturated systems and, when the F's are properly interpreted,[8a] to partially dielectrically saturated systems as well. All F's refer to the same initial volume.

From Eq. (13) one obtains (14) and (15) for the polar contribution to the spectral shift of absorption, $\Delta h\nu_a$, and that of fluorescence, $\Delta h\nu_f$

$$\Delta h\nu_a=F_e-F_g+F^{\rm op}{}_{e-g}-F_{e-g}, \quad (14)$$

$$-\Delta h\nu_f=F_g-F_e+F^{\rm op}{}_{g-e}-F_{g-e}, \quad (15)$$

where e and g denote excited and ground electronic states, respectively.

Addition of these two results yields (16)

$$h\Delta(\nu_a-\nu_f)=F^{\rm op}{}_{e-g}+F^{\rm op}{}_{g-e}-F_{e-g}-F_{g-e}. \quad (16)$$

When F is an even function of the charge distribution Eq. (17) follows

$$h\Delta(\nu_a-\nu_f)=2(F^{\rm op}{}_{e-g}-F_{e-g}). \quad (17)$$

EXPRESSION FOR SHIFT IN TERMS OF GIBBS FREE ENERGIES

The Helmholtz free energy of a charged system of volume V, which may or may not equal its equilibrium volume V_e at the prevailing pressure p, is denoted by $A(T, V)$. The Helmholtz free energy of the uncharged system of volume V is $A^{(0)}(T, V)$ and its equilibrium volume is $V^{(0)}$. We introduce quantities $G(T, p, V)$ and $G^{(0)}(T, p, V)$, defined by (18) and (19). When V in (18) equals V_e, $G(T, p, V)$ is the usual Gibbs free energy of the system at the pressure p; G is then a function of T and p alone. Similar remarks apply to $G^{(0)}(T, p, V)$ when V in (19) equals $V^{(0)}$

$$G(T, p, V)=A(T, V)+pV, \quad (18)$$

$$G^{(0)}(T, p, V)=A^{(0)}(T, V)+pV. \quad (19)$$

It can be shown[18] that $G(T, p, V)-G(T, p, V_e)$ is of the order of $(V-V_e)^2$ and that

$$G^{(0)}(T, p, V)-G^{(0)}(T, p, V^{(0)})$$

is of the order of $(V-V^{(0)})^2$. Thus, it follows that when second-order terms are neglected $A(T, V)-A^{(0)}(T, V)$, which equals $G(T, p, V)-G^{(0)}(T, p, V)$ according to (18) and (19), also equals

$$G(T, p, V_e)-G^{(0)}(T, p, V^{(0)}).$$

The latter is the polar contribution to the Gibbs free energy of solvation, and contains electrostrictive effects since V_e need not be the same as $V^{(0)}$.

Since each F in Eq. (13) for the shift is by definition $A(T, V_0)-A^{(0)}(T, V_0)$, where V_0 is the volume of the initial state [0], we see that each F is also the polar contribution to the Gibbs' solvation free energy $G(T, p)-G^{(0)}(T, p)$, on neglecting the second-order terms. (We omit the V_e and $V^{(0)}$, to indicate that the equilibrium volumes are implied, as in the conventional notation.)

Somewhat more care is needed in the analysis of $F^{\rm op}$, which refers to a system not only constrained to a given volume as was F but also constrained in its response. However, $F^{\rm op}$ should be approximately the

[18] Consider for example $G(T, p, V)-G(T, p, V_e)$. This term equals $(\partial G/\partial V)_{T,p}(V-V_e)$ plus second- and higher-order terms in $(V-V_e)$, $\partial G/\partial V$ being evaluated at $V=V_e$. However, differentiation of (18) shows that $(\partial G/\partial V)_{T,p}$ equals $(\partial A/\partial V)_T+p$, which vanishes at $V=V_e$ according to a well-known thermodyamic relation. (That relation applies only at $V=V_e$, of course.) Thus, the term $G(T, p, V)-G(T, p, V_e)$ is of the order of $(V-V_e)^2$.

same for nonpolar solvents, and the major solvent effect in Eq. (13) should be on the F's. We recall that under certain conditions[19] F^{op} is exactly equal to an expression of the type (4) for a nonpolar system [one for which $U(1)$ vanishes]. These conditions are fulfilled for dielectric continuum treatments, for example.[19] Thus, $F_{1-0}{}^{op}$ in Eq. (13) is regarded as the polar contribution to the Gibbs' free energy of a nonpolar system.

BEHAVIOR OF EQ. (13) AND SOLUTE POLARITY

When the initial state is nonpolar Eq. (13) becomes

$$\Delta E_T = F_1{}^{op}, \tag{20}$$

which is insensitive to the polarity of the solvent. In this case the polar contribution to the spectral shift does not vary markedly from solvent to solvent. Thereby, one has a test of solute polarity: The polarity of the initial state is small when the shift does not vary appreciably with solvent polarity; the polarity of the final state is small when the shift of the reverse transition does not vary appreciably with solvent polarity. Consequently, the measurement of solvent shifts for both the absorption and fluorescence spectrum is desirable, when feasible.

Equation (13) also has a simple form when the final electronic state is nonpolar or, more generally, when its charge distribution is "orthogonal" to that of the initial state in a sense defined by Conditions (a) and (b):

(a)

$$\int \langle \phi_{s_i} - \phi_s{}^{(0)} \rangle \rho_{s_j}{}^{\circ} d\mathbf{r} = 0; \tag{21}$$

(b) for any configuration τ there is an equally probable one τ', such that the magnitudes of $U_i(1)$ and $U_j(1)$ are unchanged and such that either $U_i(1)$ or $U_j(1)$ changes in sign but not both, when the coordinates are transformed from τ to τ'.

In (21), $\phi_s{}^{(0)}$ is the potential at $\mathbf{r}$ for any configuration τ in a system for which $\rho_s{}^{\circ}$ is set equal to 0. In (21) $\langle\ \rangle$ is the average for the uncharged system, as in Eq. (5).

We note that all quantities appearing in Conditions (a) and (b) are linear functionals of the $\rho_s{}^{\circ}$'s: $U(1)$ is linearly dependent on the $\rho_s{}^{\circ}$ and vanishes when the $\rho_s{}^{\circ}$ vanish; $\phi_i - \phi_i{}^{(0)}$ is seen in Appendix I to have a similar property. Conditions (a) and (b) are satisfied trivially when either state is nonpolar. They are also satisfied under other situations, for example, when the charge density in the two states i and j are each represented by a dipole, but oriented along mutually perpendicular symmetry axes of a geometrically symmetrical solute molecule—an ellipsoid, sphere, cylinder, etc. (At best, such a molecule could be only approximately symmetrical, however.)

[19] For a discussion of nonpolar and optical polarization systems and of these conditions see Ref. 8(a).

When Conditions (a) and (b) are fulfilled it can be shown that (22) is obtained (Appendix I)

$$F_{1-0} = F_1 + F_0, \qquad F_{1-0}{}^{op} = F_1{}^{op} + F_0{}^{op}. \tag{22}$$

Thus, when either the final state is nonpolar (and hence when $F_1 = F_1{}^{op} = 0$, and so $F_{1-0} = F_{-0}$, $F_{1-0}{}^{op} = F_{-0}$) or when its charge distribution is "orthogonal" to that of the initial state one finds

$$\Delta E_T = F_1{}^{op} + F_{-0}{}^{op} - F_0 - F_{-0} \cong F_1{}^{op} + F_0{}^{op} - 2F_0, \tag{23}$$

$F_1{}^{op}$ vanishing for a nonpolar final state.

When $F_0{}^{op}$ is relatively constant among different solvents, it follows from (23) that differences in spectral shifts for two solvents should be equal to twice the difference of polar contribution to the solvation free energy of the initial electronic state of the solute in the two solvents. The fact that it is equal to twice the latter difference rather than to the difference itself reflects the fact that solvation lowers the energy of the polar state by an amount approximately equal to the solvation free energy but the strained state of the medium in which the excited state is formed raises the energy of the latter by an amount roughly equal to $F_0{}^{op} - F_0$. It should be noted that $F_0{}^{op}$ and F_0 are both negative, that $|F_0| > |F_0{}^{op}|$, and that $F_0{}^{op} - F_0$ is a "strain" term, for it vanishes when the solvent is not capable of orientation or vibrational polarization.

In the case of a diphenyl betaine molecule,[4] where the formal charges are an O^- at one end of the molecule and an N^+ in the center, with the two separated by a phenyl group, the ΔE_T in water minus that in isooctane is 26 kcal mole^{-1}. In the case of a substituted pyridinium iodide[9] this difference is 34 kcal mole^{-1}. Under the assumption of a nonpolar excited state, the corresponding polar contribution to the free energy of solvation of the two dipolar compounds in water is thereby estimated to be -13 and -17 kcal mole^{-1}, respectively. Some caution here and later should be observed, however, for hydrogen-bonded solvents if a local saturation effect occurs; the interpretation of F_{1-0}, and, hence, of F_{-0}, becomes more complex then. An alternative description for the nearest-neighbor solute–solvent interaction could be preferable in that case.

If, instead, one assumes that the presumably small[9] dipole moment in the excited state of the pyridinium iodide is not actually zero but is finite though perpendicular to that of the ground state, Eq. (23) still applies, and so, therefore, does the estimated polar contribution of -17 kcal mole^{-1} to the solvation free energy of the ground state.

EQUATION FOR THE BROADENING

The fluctuation term in Eq. (12) appears in Eq. (16) of Ref. 8(a) in an incidental way. On combining that equation with Eq. (7) there we find

$$\delta^2 = 2kT(F^{non} - F_1), \tag{24}$$

where F^{non} is the polar contribution to the free energy of a system having the charge distribution [1] and having an orientation polarization appropriate to the initial state [0]. The rhs has been evaluated in Ref. 8(a), namely in Eq. (14) there for dielectrically unsaturated systems or in Eq. (18) for partially saturated systems. In either case we find

$$\delta^2 = 2kT(F_{1-0}^{\text{op}} - F_{1-0}), \tag{25}$$

where proper interpretation is to be given to the F's when partial saturation occurs. When there is a change-of-polarizability term in $F^{\text{non}} - F_0$ it is simply to be added to $F_{1-0}^{\text{op}} - F_{1-0}$, since the above derivation of (24) did not neglect this possibility.

If δ_a^2 and δ_f^2 denote the broadening for the absorption and fluorescence spectra, respectively, then one obtains from (16) and (25) an equation connecting broadening and spectral shift

$$\delta_a^2 + \delta_f^2 = 2kTh\Delta(\nu_a - \nu_f). \tag{26}$$

Some particular cases arise: (1) when F is an even function of the charge distribution Eq. (25) shows that δ_a^2 and δ_f^2 are equal

$$\delta_a^2 = \delta_f^2; \tag{27}$$

(2) when the ground state is polar and the excited state is not, it was noted earlier, the absorption spectrum but not the fluorescence spectrum will be shifted by changing the solvent polarity (and conversely). In this case $\Delta\nu_f$ is relatively independent of solvent polarity. When F is an even function of the charge distribution we then obtain (28) relating the difference in δ_a^2 and in $\Delta\nu_a$ for two solvents

$$\Delta\{\delta_a^2\} = \Delta\{kTh\Delta\nu_a\}. \tag{28}$$

APPLICATION TO THE DATA ON BROADENING

If the electronic transition moment is roughly constant over the band, the mean-square energy difference of initial and final states, appearing on the lhs of (11), equals a mean-square "half-bandwidth," as defined below. One normally measures instead the bandwidth at half-maximum. If in the neighborhood of its maximum an absorption or fluorescence band is approximately a Gaussian function of x, the distance from the maximum, the intensity at x is proportional to $\exp(-x/\sigma)^2$. In this case the root-mean-square half-bandwidth $\langle x^2\rangle^{\frac{1}{2}}$ is readily found to be $\sigma/\sqrt{2}$ and the half-bandwidth at half-maximum to be $\sigma(\ln_e 2)^{\frac{1}{2}}$. The latter therefore equals the former multiplied by 1.2. The bandwidth therefore equals 2.4 times $\langle x^2\rangle^{\frac{1}{2}}$, the quantity appearing on the lhs of (11).

We make the correlation assumption embodied in Eq. (11). It then follows that the mean-square half-bandwidth is the sum of a polar term and of a nonpolar term. The latter arises in part from the vibrational fluctuations of the solute, and we assume thereby that correlations of the solute vibrations and solvent rotations can be ignored.

Dimroth and co-workers have recently published spectra of some betaines[4] to which the present results may be applied. For example, the absorption maximum of betaine-26 in methanol is shifted from that in dioxane by about 6000 cm^{-1}. Dimroth and co-workers point out that the excited state should be relatively nonpolar. Equation (28) may then be applied. At room temperature the difference in mean-square half-bandwidths in the two solvents computed from this equation is 1100 cm^{-1}. Hence the predicted difference in width at half-maximum in the two solvents is 2600 cm^{-1}.

Because of the presence and distorting effect of another band on the short-wavelength side we do not estimate the bandwidths from the spectra directly. Rather, it is better to estimate the half-bandwidth at half-maximum, namely, the half-width on the long wavelength side. From this difference the bandwidth at half-maximum in the two media is estimated to be about 2500 cm^{-1}, in good accord with the predicted value. Somewhat analogous remarks apply to a comparison of betaine-1 in *tert*-butyl alcohol, methanol, and water, though not for betaine-30 in ethanol and in water, but we omit the details.

The total bandwidth at half-maximum found experimentally from the spectral shape in the above way is about 3000 to 5000 cm^{-1} in a relatively nonpolar medium. (Only a few curves were published, however.) It would be desirable for the fractional share of the polar contribution to be larger, if Eq. (28) is to be tested more accurately. If a system can be found in which the vibrational potential-energy functions are sufficiently similar, the width can be reduced somewhat. The bandwidth for merocyanines in a suitable polar solvent is as small as 2000 cm^{-1}, and is itself perhaps due principally to the polar interactions. The narrowness of the band was ascribed[20] to the above behavior of the vibrational functions, an argument that was supported by other evidence.[20]

THEORIES AND DATA ON SPECTRAL SHIFTS

The present work can be used to assess the very interesting results of Ooshika[1] and McRae[3] obtained by more approximate methods. As noted earlier these authors used quantum-mechanical perturbation theory and then estimated the averages of various polar terms by treating the solvent as a dielectric continuum. The solute molecule was treated as a sphere containing a polarizable point dipole. Several additional approximations were introduced to facilitate the involved manipulations. The latter approximations and that of a point-dipolar solute in a sphere are absent in the present treatment. The approximation of a dielectric continuum also has not been introduced yet.

[20] J. R. Platt, J. Chem. Phys. **25**, 80 (1956); cf. Ref. 3(b). Both this article and Ref. 3(b) contain extensive references to the two-resonant structure theory of the merocyanines, which explains a large polarizability effect.

Ooshika's results were later simplified by Lippert,[2] who omitted the dispersion terms and set the solute polarizability equal to zero. Application of this modified Ooshika equation permitted Lippert to calculate dipole moments of excited states from data on spectral shifts.[2] McRae has used his treatment to explain the interesting reversal in spectral shift with solvent polarity for the merocyanines, by assuming an appreciable difference in polarizability of ground and excited states and considering a quadratic Stark effect.[3]

Equation (13) can be used to compute spectral shifts and to include the change-of-polarizability effect just mentioned. Thus, all of these results can be compared directly. For completeness, we give in Appendix II the F values for a variety of solute models which have been used in the literature to calculate polar interactions by treating the solvent by a dielectric continuum, and which can now be applied to the present problem of spectral shifts. Alternatively, a statistical-mechanical model can be used to calculate the F's appearing in Eq. (13).

Upon applying the models in Appendix II and comparing the results with Ooshika's, McRae's, and Lippert's one finds:

(1) When the polarizability of the solute molecule is set equal to zero, the results of McRae and Ooshika for the polar term are in agreement with each other and in agreement with those computed from Eq. (13) when the sphere-dipole model is introduced in the latter to compute the F's. This model was used by Lippert.[2a]

(2) When the polarizability of the solute molecule in its initial and final electronic states is not taken to be zero but is taken to be the same, the results of McRae and Ooshika disagree. If in Eq. (13) one introduces this same point-dipole model, the result agrees with that obtained by Ooshika to first order in the polarizability.[21] The source of disagreement in higher terms is the neglect of successive effects of the polarized dipole on the reaction field in the earlier work.

(3) When the polarizability of the solute is different in the initial and final states there appears to be no agreement. This term was, in fact, the most difficult one to evaluate and requires an elaborate calculation. The result in Ref. 8(a) is correct to first-order differences in polarizability (for the given initial approximations, without containing the additional ones introduced by McRae and Ooshika). It is given later by Eq. (30). Its particular value for the polarizable point dipole in a sphere model, embedded in dielectric continuum, is given in Eq. (37).

(4) When there is an appreciable separation of charge in the polar solute the use of a point-dipole model can lead to appreciable error, as discussed in Appendix II.

(5) If one considers a somewhat more general shape than a sphere for the solute, an ellipsoid for example, and introduces the value of F for this model one obtains some estimate of the error involved in using a sphere, as in Appendix II or in Ref. 2(b). The error can either be reduced, the calculations show, by treating the ellipsoid as a sphere whose diameter is approximately the major axis of the ellipsoid, $2a$ in the case of a molecule whose dipole moment is oriented along this axis, or simply by treating this molecule as an ellipsoid.

(6) On using the data obtained by Kosower[9] for pyridinium iodide in polar solvents and using the model of separated charges, it is estimated from the separated-charge formula that only the dipolar contribution is appreciable. From the spectral data, the polar contribution to the free energy of solvation of the ion-pair ground state is estimated to be -17 kcal mole^{-1}, with the aid of Eq. (23), as noted earlier. The dipole moment estimated from this solvation free energy and Eq. (A11) is about 10 D, a not unreasonable value.

(7) While McRae's interesting interpretation of the reversal of spectral shift with solvent polarity for the merocyanines may be qualitatively correct, the quantitative results need correction, due to the discrepancies noted in Secs. 3 and 4. In the case of the "polarizable point-dipole-in-a-sphere" model used by McRae the new expression for the shift is given in the following section. There exists a two-resonant structure explanation of this (presumed) large polarizability difference of initial and final states of merocyanine.[20]

REVERSAL OF SPECTRAL SHIFT DUE TO POLARIZABILITY DIFFERENCES

On using Eqs. (9), (15), and (35) of Ref. 8(a), the polar contribution to the spectral shift is given by (29), to first order in the polarizability operator difference, $A_{s1}-A_{s0}$

$$\Delta E_T=\Delta+\Delta_\alpha, \tag{29}$$

where Δ is the normal term and Δ_α is the term due to a polarizability operator difference in initial and final

[21] Correction is made for several typographical errors [Ooshika (private communication)] in Ooshika's basic equation (the first one in Sec. 3 of Ref. 1): The μ_e^2 in the first line should be replaced by $(\mu_e^2+\mu_g^2)/2$ and a $2(n^2-1)$ the last term but 1 should be replaced by n^2-1.

In making the comparison with the corrected equation, we observe that his

$$\sum_{m\neq g}(g\mid \mathbf{\mu}_0\mid m)^2/(\epsilon_m-\epsilon_g)$$

and

$$\sum_{m\neq e}(e\mid \mathbf{\mu}_0\mid m)^2/(\epsilon_m-\epsilon_e)$$

equals $\alpha_g/2$ and $\alpha_e/2$, respectively, and that his

$$\sum_{m\neq g}[\mathbf{\mu}_g(g\mid \mathbf{\mu}_0\mid m)]^2/(\epsilon_m-\epsilon_g),$$

$$\sum_{m\neq g}[\mathbf{\mu}_g(e\mid \mathbf{\mu}_0\mid m)]^2/(\epsilon_m-\epsilon_g),$$

and

$$\sum_{m\neq g}[\mathbf{\mu}_g(g\mid \mathbf{\mu}_0\mid m)][\mathbf{\mu}_e(g\mid \mathbf{\mu}_0\mid m)]/(\epsilon_m-\epsilon_g)$$

equals $\mathbf{\mu}_g\cdot\mathbf{\mu}_g\alpha_g/2$, $\mathbf{\mu}_g\cdot\mathbf{\mu}_g\alpha_e/2$ and $\mathbf{\mu}_g\cdot\mathbf{\mu}_e\alpha_g/2$. [For typographical reasons, Ooshika's letters with arrows have been replaced by boldface letters. The dots in the scalar product were not specified, but examination of Eqs. (14) and (15) there and of his equation just preceding Eq. (27) suggests the choice just adopted.] The final two terms in the cited basic equation can be identified as dispersion terms. The principal shortcoming lies in third term involving $\alpha_e-\alpha_g$; it contains an additional approximation.

electronic states[22]

$$\Delta_\alpha=\left(\frac{\partial F_{1-0}{}^{\mathrm{op}\gamma}}{\partial\gamma}\right)_{\gamma=0}+\left(\frac{\partial F_0{}^{\gamma}}{\partial\gamma}\right)_{\gamma=0}$$
$$+\sum_s\int\langle\phi_{s1-0}{}^{\mathrm{op}}\rangle_{1-0,\mathrm{op}}\Delta A_s\langle\phi_{s0}\rangle_0 d\mathbf{r}, \quad (30)$$

where the polarizability operator $A_s{}^\gamma$ in $F_{1-0}{}^{\mathrm{op}}$ and F_0 is

$$A_s{}^\gamma=A_{s0}+\gamma(A_{s1}-A_{s0}), \quad (31)$$

and where $\langle\phi_{s0}\rangle_0$ and $\langle\phi_{1-0}{}^{\mathrm{op}}\rangle_{1-0,\mathrm{op}}$ are the values of ϕ_s at the point $\mathbf{r}$ in the [0] and [1-0, op] systems, each averaged over the equilibrium statistical-mechanical configurations in the respective systems. (In dielectric continuum theory such a $\langle\phi_s\rangle$ becomes the potential $\psi(\mathbf{r})$ minus the contribution directly due to particle s.)

For illustration and comparison with earlier work the value of Δ_α is given below for a solute treated as being a sphere of radius a, as having a permanent point dipole of moment $\boldsymbol{\mu}$ and the usual induced point-dipole polarizability, α, and as being imbedded in a dielectric continuum. For this model we have[8a]

$$\rho_s{}^\circ(\mathbf{r})=-\nabla_r\delta(\mathbf{r}-\mathbf{r}_s)\cdot\boldsymbol{\mu}, \quad (32)$$

$$A_s(\mathbf{r},\mathbf{r}')=\nabla_r\delta(\mathbf{r}-\mathbf{r}_s)\cdot\alpha\nabla_{r'}\int d\mathbf{r}'\delta(\mathbf{r}'-\mathbf{r}_s), \quad (33)$$

where $\mathbf{r}$ is any point in the system and where $\mathbf{r}_s$ is the position of the permanent and of the induced dipole. In this case the last term of (30) becomes[8a]

$$-\langle\nabla\phi_{s1-0}\rangle_{1-0,\mathrm{op}}(\alpha_1-\alpha_0)\langle\nabla\phi_{s0}\rangle_0. \quad (34)$$

Each $-\langle\nabla\phi_s\rangle$ is the reaction field of the solute s which, in the absence of external electric fields, equals[8a] $f\boldsymbol{\mu}/(1-f\alpha)$, where

$$f=(1/a^3)[2(D-1)/(2D+1)]. \quad (35)$$

On using the value of F for this model given in Appendix II the following results are obtained[23]:

$$\Delta=-[f^*\boldsymbol{\mu}_0+\tfrac{1}{2}f^*_{\mathrm{op}}(\boldsymbol{\mu}_1-\boldsymbol{\mu}_0)]\cdot(\boldsymbol{\mu}_1-\boldsymbol{\mu}_0), \quad (36)$$

$$\Delta_\alpha=-\tfrac{1}{2}[f^*\boldsymbol{\mu}_0+f^*_{\mathrm{op}}(\boldsymbol{\mu}_1-\boldsymbol{\mu}_0)]^2(\alpha_1-\alpha_0), \quad (37)$$

with

$$f^*=f(1-f\alpha)^{-1}, \qquad f^*_{\mathrm{op}}=f_{\mathrm{op}}(1-f_{\mathrm{op}}\alpha)^{-1}, \quad (38)$$

where

$$f_{\mathrm{op}}=2(D_{\mathrm{op}}-1)/a^3(2D_{\mathrm{op}}+1), \quad (39)$$

and where $\boldsymbol{\mu}_0$ and $\boldsymbol{\mu}_1$ are the values of $\boldsymbol{\mu}$ in the initial and final states and α_0 and α_1 are the polarizabilities of the solute in these states.

When the final state is less polar than the initial one, Δ is positive for a polar medium and increases with increasing solvent polarity. Since α_1 is greater than α_0 if 1 refers to an excited state, while μ_1 in (36) is less than μ_0 in magnitude and f^*-f is positive, Δ_α is a term of opposite sign to Δ; Δ_α then increases quadratically with solvent polarity (i.e., with $f^*-f^*_{\mathrm{op}}$) while Δ increases only as the first power. However, initially Δ is normally larger than Δ_α. The maximum shift occurs when $\partial\Delta E_T/\partial f^*$ vanishes, i.e., when (40a) obtains

$$\boldsymbol{\mu}_0\cdot\{(\boldsymbol{\mu}_1-\boldsymbol{\mu}_0)+[f^*\boldsymbol{\mu}_0+f^*_{\mathrm{op}}(\boldsymbol{\mu}_1-\boldsymbol{\mu}_0)](\alpha_1-\alpha_0)\}=0. \quad (40a)$$

If the primary dipole moments $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_0$ can be estimated then (40a) permits some estimate of $\alpha_1-\alpha_0$ to be made from the data, but with caution because of the approximations inherent in the point-dipole-in-a-sphere model. More elaborate models, such as those in Appendix I, could be introduced into (30) instead. This reversal of solvent shift would thereby provide information on polarizabilities of excited states, if McRae's interpretation[3b] is qualitatively correct.

In studying the spectral-shift reversal, solvent mixtures of varying composition were used. Because of the possibility of selective solvation, the calculation of f^* in Eq. (35) from the bulk dielectric constant of a solution is uncertain. Some rough estimate of the f^* for a mixture might be obtained by examining its shift of the spectrum of a solute for which no spectral reversal occurs but which also has roughly the same dipole moment as the original solute. By means of a calibration curve obtained with pure solvents the f^* for a selectively solvated solvent mixture might then be obtained.

When the polarizability α_0 is not known, it may be convenient to regard the solute in the way it was regarded in some early work in solvent–solute interactions, namely as a medium of low dielectric constant, D_i.[24] It has been shown[7b] that the formalism is similar to one based on α_0, to the leading induced moment term (i.e., to the induced dipole term), provided α_0 is replaced by a function of D_i which depends on the size and shape of the solute. For a sphere we have[7b]

$$D_i=(a^3+2\alpha)/(a^3-\alpha). \quad (40b)$$

For an ellipsoid the corresponding result is given by Eq. (27) of Ref. 7(a). When α_0 is not known, D_i can be taken to be about 2 in the first approximation and α_0 calculated from (40b) or from the corresponding expression for the ellipsoid.

APPLICATION TO THERMOCHROMISM

A change of temperature can shift the absorption spectrum by shifting an equilibrium between two different forms or by modifying the configurational distribution of molecules in the medium. When the

[22] In obtaining (30) from Ref. 8(a) for present use we have equated the np and op systems, as one may do for a solvent-continuum treatment [and for some other systems, Ref. 8(a)].

[23] Compare Eq. (42) of Ref. 8(a).

[24] For example, (a) J. G. Kirkwood and F. H. Westheimer, J. Chem. Phys. **6**, 506 (1938); (b) F. H. Westheimer and J. G. Kirkwood *ibid.* p. 513

latter is the principal effect, the polar contribution to the temperature coefficient of the shift found from (13), on recalling the relation of the F's to Gibbs free energies, is

$$-(\partial\Delta E_T/\partial T)_P = S_1 - S_0 + S_{1-0}^{op} - S_{1-0}, \quad (41)$$

where the S's are the polar contributions to the entropies of the systems cited. S_{1-0}^{op} is negligible. When the final state is nonpolar S_1 vanishes and S_{1-0} becomes S_{-0}. When F (and hence S) is an even function of the charge distribution, the expression becomes

$$-(\partial\Delta E_T/\partial T)_P = -2S_0. \quad (42)$$

Equation (42) also applies when the final charge distribution and the initial one are "orthogonal" in the sense defined earlier, as one may show by differentiation of (23) on assuming S to be an even function as before.

From data obtained for betaine-30, there would not appear to be any simple correlation between $(\partial\Delta E_T/\partial T)_P$ and ΔE_T. If the nonpolar contribution to the temperature shift is given by some analog of (41), this lack of correlation supports the contention that entropies of solvation are more sensitive to nonpolar effects than are free energies.

When the temperature effects, $d\nu_{max}/dT$, for the least polar and the most polar (alcoholic) are subtracted, the difference in $d\nu_{max}/dT$ for diphenyl betaine is about 10 $cm^{-1}\cdot deg^{-1}$. If this difference is largely $-2S_0$, the polar contribution to the entropy of solvation is about -15 eu at room temperature. Some knowledge of a nonpolar contribution to $d\nu/dT$ is obtainable when one state is nonpolar and the $d\nu/dT$ is measured for a transition starting from that state.

EFFECT OF PRESSURE ON THE SPECTRAL SHIFT

The spectral shift depends on pressure partly because of a difference in size of the solute in its initial and final electronic state and partly because of a difference in electrostrictive effects. The second of these causes is due to a difference in polarity of the solute in the two electronic states, and we consider its contribution.

Upon differentiating (13) with respect to p and recalling the relation of the F's to Gibbs free energies we obtain

$$(\partial\Delta E_T/\partial p)_T = V_1 - V_0 + V_{1-0}^{op} - V_{1-0}, \quad (43)$$

where the V's are the polar contributions to the volume of solvation of the solute in the [1], [0], [1−0, op], and [1–0] systems.

When the initial and final charge distributions are "orthogonal" Eq. (43) becomes (44), on assuming $V_0 = V_{-0}$,

$$(\partial\Delta E_T/\partial p)_T = V_1^{op} + V_0^{op} - 2V_0. \quad (44)$$

If the nonpolar contribution to the pressure effect, $d\nu_{max}/dp$, were solvent independent or were small (and it may not be) then the value of $\partial\Delta E_T/\partial p$ for a polar solvent minus that for a nonpolar one would be $-2(V_0 - V_0^{op})$. If one state were nonpolar a measurement of $d\nu/dp$ for a transition starting from that state would provide some information on the magnitude of a nonpolar term.

A dielectric continuum estimate of the relation between $\partial\Delta E_T/\partial p$ and $\partial\Delta E_T/\partial T$ may be made as follows: The volumes appearing in (44) can be calculated by differentiating the F's appearing in Eq. (13), bearing in mind the relation of F's to Gibbs' free energies. However, we note that the ratio of a V to the corresponding S is independent of the solute model when the solvent is treated as a dielectric continuum

$$\frac{V}{S} = -\frac{dF/dD}{dF/dD}\frac{\partial D/\partial p}{\partial D/\partial T} = -\frac{(\partial D/\partial p)_T}{(\partial D/\partial T)_P}.$$

The value of $\partial\Delta E_T/\partial p$ for a polar solvent minus that for a nonpolar one was $-2(V_0 - V_0^{op})$, while the value of $\partial\Delta E_T/\partial T$ was $2(S_0 - S_0^{op})$. Thus, when V_0^{op} and S_0^{op} are negligible we obtain (45) for "orthogonal" charge distributions, *but only when the nonpolar contributions in the numerator cancel and those in the denominator cancel*

$$\frac{(\partial\Delta E_T/\partial p)_{polar} - (\partial\Delta E_T/\partial p)_{nonpolar}}{(\partial\Delta E_T/\partial T)_{polar} - (\partial\Delta E_T/\partial T)_{nonpolar}} \simeq \frac{(\partial D/\partial p)_T}{(\partial D/\partial T)_P}. \quad (45)$$

The value of the ratio on the right is roughly about -0.013 deg atm^{-1} for ethanol.[25] Since $\partial\Delta E_T/\partial T$ for diphenyl betaine was about 10 $cm^{-1}\cdot deg^{-1}$; as noted earlier, one would predict from (45) that

$$(\partial\Delta E_T/\partial p)_{polar} - (\partial\Delta E_T/\partial p)_{nonpolar}$$

would be about -0.15 $cm^{-1}\cdot atm^{-1}$. There appear to be no measurements of the pressure effects with polar solutes for which the temperature effect has also been measured.

EFFECT OF ELECTRIC FIELDS ON THE SPECTRAL SHIFT

An electric field can affect the spectral shift by interacting differently with the permanent dipole of the solute in the initial and final state and by inducing a different dipole in the two states when the polarizabilities in the initial and final states differ. Equation (13) applies as before,[8] but now the calculation of each F is made for the solute having any given orientation of the solute in the electric field. Broadening should occur because of the Boltzmann distribution of solute orientation in the applied field. The contribution of the solute polarizability difference to the electric field effect may be computed by employing (13), (29), and

[25] *Landolt-Börnstein Tabellen*, edited by K. H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, 1959), 6th ed., Vol. II, Part 6, pp. 678–689.

(30) and taking the presence of the electric field into account. We consider, for simplicity, the point-dipole-in-a-sphere model described earlier. However, more complex models, such as the others in Appendix II, could be used instead.

The F_{1-0} in Eq. (13) depends only on the difference of the permanent charge distributions in the [0] and [1] systems. Since the permanent charge distribution on the electrodes cancels in computing this difference, the latter electrode charge does not affect F_{1-0}. Similarly it has no effect on F_{1-0}^{op} or on $\langle\phi_{s1-0}^{op}\rangle$ in Eq. (30). For the value of any other F it is convenient to use (46)[26]

$$F_k=\tfrac{1}{2}\sum_s\left(\int\langle\phi_{sk}\rangle_k\rho_{sk}^{\circ}d\mathbf{r}+\int\langle\phi_s^{(0)}\rangle\rho_{sk}^{\circ}d\mathbf{r}\right), \quad (46)$$

where $k=1$ or 0.

In the present case there are three s's, namely the solute and the two electrodes. The solvent is treated as a dielectric continuum in this section in the standard way; $\langle\phi_s^{(0)}\rangle$ in (46) vanishes in this approximation. For the dipolar solute ρ_s° is given by (32) and A_s by (33). For one plane electrode ρ_s° is $\sigma^0\delta(x)$, and for the other ρ_s° is $-\sigma^0\delta(x-L)$, where σ^0 is the "permanent" surface charge density of the first electrode,[27] x is the coordinate normal to the two plane-parallel electrodes, and the latter are situated at $x=0$ and $x=L$. The A_s of each electrode in the present discussion is such as to give rise to the usual electrostatic image charge distribution.[28]

When the solute is far from the electrode the influence of the electrode image charge on the dipole vanishes, and the field inside the sphere is found from standard electrostatics to be the sum of two terms[29]: a nonuniform field from the net dipole of the solute $\mathbf{m}$ and a uniform field R from the electrodes and the polarized medium. The net field inside the sphere is derivable from a potential $\psi(\mathbf{r})$, given by (50)

$$m=\mathfrak{y}+\alpha\mathbf{R}, \quad (47)$$

$$R=g\mathbf{E}_\infty+f\mathbf{m}, \quad (48)$$

where f is given by (35) and

$$g=3D/(2D+1), \quad (49)$$

$$\psi(\mathbf{r})=(\mathbf{m}\cdot\mathbf{r}/r^3)-\mathbf{R}\cdot\mathbf{r} \qquad (r\leq a). \quad (50)$$

In the above equations $\mathfrak{y}$ is the "permanent" dipole, i.e., the value of $\mathbf{m}$ at zero field $\mathbf{R}$, and $\mathbf{E}_\infty$ is the applied field, i.e., $E_\infty L$ is the potential drop in the solution between the electrodes.

The potential outside the sphere is found to be the sum of two terms: one associated with a nonuniform field arising from an apparent dipole moment $\mathbf{M}$ and the other directly associated with the uniform applied field $\mathbf{E}_\infty$[30]

$$\psi(\mathbf{r})=(\mathbf{M}\cdot\mathbf{r}/r^3)-\mathbf{E}_\infty\cdot\mathbf{r}, \qquad (r\geq a), \quad (51)$$

where

$$\mathbf{M}=(g\mathbf{m}/D)-(a^6f\mathbf{E}_\infty/2). \quad (52)$$

From (47) and (48) one finds

$$\mathbf{R}=f^*\mathfrak{y}+g^*\mathbf{E}_\infty, \quad (53)$$

where

$$g^*=g/(1-\alpha f). \quad (54)$$

In (46) we consider first the s which refers to the dipole, and recall that its ρ_s° is related to $\mathfrak{y}$ as in (32). The value of $\langle\phi_{sk}\rangle_k$ for this s is obtained by subtracting from (49a) $\mathbf{m}\cdot\mathbf{r}/r^3$. One then finds $-\frac{1}{2}\mathfrak{y}\cdot\mathbf{R}$ for this contribution to the first term of (46). We consider next the s referring to the first electrode. The $\langle\phi_{sk}\rangle_k$ is obtained from the electrostatic potential (49b) by subtracting a term $\psi_\sigma^{(1)}$ which is proportional to σ^0 and which is independent of D and $\mathfrak{y}$. On recalling that ρ_s° for this s is $\sigma^0\delta(x)$ and using a symmetry theorem[31] for charge distributions we find that the contribution for this s to the first term of (46) is $-\frac{1}{2}\mathbf{M}\cdot\mathbf{E}_\sigma^{(1)}-\frac{1}{2}\int\sigma^0(\psi_\infty-\psi_\sigma^{(1)})dA$, where $\mathbf{E}_\sigma^{(1)}$ is $-\nabla\psi_\sigma^{(1)}$, ψ_∞ is the applied potential at $x=0$ (at $x=L$ it will be $\psi_\infty-E_\infty L$), and integration is over the electrode area A which in the final answer for the spectral shift we allow to become infinite. Similarly, the corresponding term in (46) for s being the second electrode is

$$-\tfrac{1}{2}\mathbf{M}\cdot\mathbf{E}_\sigma^{(2)}+\frac{1}{2}\int\sigma^0(\psi_\infty-E_\infty L-\psi_\sigma^{(2)})dA.$$

[26] Equation (46) is deduced in Appendix III. It may be compared formally with the usual dielectric continuum expression: $\langle\phi_{sk}\rangle_k$ is the usual macroscopic electrostatic potential at r minus the self-potential of s. It is also the microscopic potential at r minus the self-potential of s, averaged over the equilibrium statistical-mechanical distribution of configurations τ of the solvent molecules. When one of the typical approximations in continuum theory is made, namely of neglecting $\langle\phi_s^{(0)}\rangle$ in the hypothetical system for which ρ_s° vanishes, Eq. (46) formally resembles the usual[8a] continuum expression, without containing the continuum approximation as yet. The latter can then be introduced, as in Eq. (50).

[27] That is, σ° is the charge density for the given potential drop across the electrodes and for the given medium, but excluding any contribution from the image charge arising from the specified solute molecule.

[28] When a particle (such as an electrode, a medium, or a solute) is treated as a continuum, as it often is, the functional equation relating the induced charge density ρ^{in} to A_s still applies but now A_s has a value found from standard electrostatics.[7b] If one uses electrostatics, as we do in obtaining (50), ρ^{in} for the electrode is then obtained from the usual image charge calculation. When the solute is far from the electrode, as in the present case, the influence of ρ^{in} vanishes, and so we can ignore it.

[29] For example, W. F. Brown, Jr., *Encyclopedia of Physics*, edited by S. Flugge (Springer-Verlag, Berlin, 1955), Eqs. (9.4) (9.14), and (26.2). We use units for which $\gamma=4\pi$ there.

[30] Reference 28, Eqs. (8.8), (9.5), and (9.15).

[31] For two specified charge distributions ρ_i and ρ_j we have

$$\int\rho_i(\mathbf{r})\psi_j(\mathbf{r})d\mathbf{r}=\int\int\rho_i(\mathbf{r})\rho_j(\mathbf{r}')r^{-1}d\mathbf{r}\,d\mathbf{r}'=\int\rho_j(\mathbf{r})\psi_i(\mathbf{r})d\mathbf{r},$$

where

$$\psi_i(\mathbf{r})=\int\rho_j(\mathbf{r}')r^{-1}d\mathbf{r} \quad \text{and} \quad r=|\mathbf{r}'-\mathbf{r}'|.$$

In applying this result to one term in the example just cited, ρ_i corresponds to the charge density of one of the electrodes and ρ_j to a solute hypothetical dipole moment M.

Upon adding these results, noting that $\mathbf{E}_\sigma^{(1)}+\mathbf{E}_\sigma^{(2)}$ equals $D\mathbf{E}_\infty$, and that $\int\psi_\sigma^{(2)}\sigma^0 dA$ equals $-\int\psi_\sigma^{(1)}\sigma^0 dA$, we obtain

$$F=-\tfrac{1}{2}\mathfrak{y}\cdot\mathbf{R}-\tfrac{1}{2}D\mathbf{M}\cdot\mathbf{E}_\infty-\frac{1}{2}\int\sigma^0(E_\infty L-2\psi_\sigma^{(1)})dA. \quad (55)$$

This result is to be introduced into (29) and (30).

We also note that the only s which contributes to the last term in (30) is that for the solute molecule. This term then becomes[8a]

$$-(\alpha_1-\alpha_0)\mathbf{R}_{1-0}{}^{\mathrm{op}}\cdot\mathbf{R}_0, \quad (56)$$

where the $\mathbf{R}_0$ is given by (53) with $\mathfrak{y}$ replaced by $\mathfrak{y}_0$ and where $\mathbf{R}_{1-0}{}^{\mathrm{op}}$ is given by (53) with $\mathbf{E}_\infty=0$, $\mathfrak{y}$ replaced by $\mathfrak{y}_1-\mathfrak{y}_0$, α by α_0, and f by f^{op}.

On performing the differentiation indicated in Eq. (30), and subtracting from the final expression for the shift the value of the shift when E_∞ vanishes we obtain (57)

$$\Delta E_T(E_\infty)-\Delta E_T(E_\infty=0)=-g^*\mathbf{E}_\infty\cdot\{\mathfrak{y}_1-\mathfrak{y}_0+(\alpha_1-\alpha_0)\times[\mathfrak{y}_0 f^*+\tfrac{1}{2}\mathbf{E}_\infty g^*+(\mathfrak{y}_1-\mathfrak{y}_0)f^*{}_{\mathrm{op}}]\}, \quad (57)$$

where f^*, $f^*{}_{\mathrm{op}}$, and g^* are given by (38) and (54).

The shift depends on the orientation of the original solute dipole. The part of the reversible work (52) of formation of the dipole in the medium which depends on the orientation is

$$\Delta F(\theta)=-g^*\mathfrak{y}_0\cdot\mathbf{E}_\infty, \quad (58)$$

where θ is the angle between $\mathfrak{y}_0$ and $\mathbf{E}_\infty$. The probability of finding θ in θ, $\theta+d\theta$ is

$$\exp\left(-\frac{\Delta F(\theta)}{kT}\right)\sin\theta d\theta \Big/ \int_{\theta=0}^{\pi}\exp\left(-\frac{\Delta F(\theta)}{kT}\right)\sin\theta d\theta \quad (59)$$

when the dipole is free to orient itself. When $\Delta F(\theta)/kT$ is comparatively small or when no reorientation is possible because of a rigid solid solvent, the orientation in the presence of the external field E_∞ is random, so that the θ-dependent terms in (57) contribute to the broadening rather than to the spectral shift. In this case, the averaging function is $\sin\theta d\theta/2$ instead of (59) and one finds

$$\Delta E_T(E_\infty)-\Delta E_T(E_\infty=0)\cong-\tfrac{1}{2}(\alpha_1-\alpha_0)g^{*2}\mathbf{E}_\infty{}^2. \quad (60)$$

When instead $\Delta F(\theta)/kT$ is not negligible but is still small the contribution of the other terms in (57) to the mean spectral shift is obtained by multiplying by (57), expanding $\Delta F(\theta)$ and integrating over θ. It turns out to be proportional to $\mathbf{E}_\infty{}^2/kT$.

Some experiments on the influence of electric fields have been made by Kumamoto, Powers, and Heller,[14] who studied the absorption spectrum of methyl red imbedded in a nonpolar solid (polystyrene) and employed electric fields of about 10^6 V cm^{-1}, and found the shift to be about 10 Å for the 5000-Å absorption band. They found the shift to be proportional to $\mathbf{E}_\infty{}^2$, and noted that some broadening would occur because of permanent dipolar effects. They found little broadening and suggested that the dipole moments were not large and did not change markedly between initial and excited states. In this case the shift would be given by Eq. (60). From a knowledge of the dielectric constant of polystyrene an estimate of $\alpha_1-\alpha_0$ can be made from the data. Alternatively, a model such as an ellipsoidal one could have been used instead.

The electrochromic effect studied by these authors should provide information on the reversal-shift effect noted earlier and embodied in Eqs. (36) and (37). It would be particularly helpful to investigate the two effects for the same solute. A relation between them may be examined with the aid of the above equations.

APPENDIX I. PROOF OF EQ. (22) FOR "ORTHOGONAL" CHARGE DISTRIBUTIONS

We first note and later prove that $U(1)$, $U(2)$, and the polar contribution to $U(0)$, $U^{\mathrm{pol}}(0)$, are given by (A1) to (A3)

$$U^{\mathrm{pol}}(0)=\frac{1}{2}\int\rho_M{}^\circ\phi_M{}^{(0)}d\mathbf{r}, \quad (A1)$$

$$U(1)=\sum_s\int\rho_s{}^\circ\phi_s{}^{(0)}d\mathbf{r}, \quad (A2)$$

$$U(2)=\tfrac{1}{2}\sum_s\int\rho_s{}^\circ\eta_s d\mathbf{r}, \quad (A3)$$

where

$$\eta_s=\phi_s-\phi_s{}^{(0)}. \quad (A4)$$

On using Eq. (10) of Ref. 8(a) for F_{1-0}, F_1, and F_{-0} and on using (A3) for their $U(2)$'s, one finds

$$F_{1-0}-F_1-F_{-0}=\sum_s\left\langle\int\rho_{s1}{}^\circ\eta_{s-0}d\mathbf{r}\right\rangle - (1/kT)[\langle U_1(1)U_{-0}(1)\rangle-\langle U_1(1)\rangle\langle U_{-0}(1)\rangle], \quad (A5)$$

where the subscript -0 denotes a system having a charge distribution $-\rho_{s0}{}^\circ$ on the s's. In deducing (A5) use was made of (A6) and also of the fact that the $U(1)$'s are linear functionals of the $\rho_s{}^\circ$ [i.e., $U_{1-0}(1)=U_1(1)+U_{-0}(1)$]

$$\sum_s\int\rho_{s1}{}^\circ\eta_{s-0}d\mathbf{r}=\sum_s\int\rho_{s-0}{}^\circ\eta_{s1}d\mathbf{r}. \quad (A6)$$

Equation (A6) itself is deduced later.

On introducing Eq. (21), i.e., on imposing Condition (a) for the "orthogonality" of charge distributions, the first term on the right-hand side of (A5) vanishes. On imposing Condition (b) the next term in (A5) vanishes, and because of the symmetry of the molecule assumed in Condition (b) both $\langle U_1(1)\rangle$ and $\langle U_{-0}(1)\rangle$ vanish.

To complete the proof it remains to establish (A1) to (A3) and (A6). If a parameter λ is introduced into the expressions (1), (2), and (3) for ϕ_i, ρ_j^{in} and U^{pol}, such that λ multiplies ρ_s° wherever it appears, and if the corresponding U^p is denoted by U^λ, we find

$$U^\lambda=\tfrac{1}{2}\sum_i \rho_i^{\circ\lambda}[\phi_i^{(0)}+(\phi_i^\lambda-\phi_i^{(0)})]d\mathbf{r}, \qquad \text{(A7)}$$

where $\rho_s^{\circ\lambda}=\lambda\rho_s^\circ$, $\rho_M^{\circ\lambda}=\rho_M^\circ$, and where $\phi_i^\lambda-\phi_i^{(0)}$ satisfies the following set of equations, obtained by subtracting Eq. (1) for ϕ_i^λ from the corresponding equation for $\phi_i^{(0)}$; the equation for $\phi_i^{(0)}$ is obtained by setting $\rho_s^\circ=0$ in (1):

$$\phi_i^\lambda-\phi_i^{(0)}=\sum_{s'\neq i}\int\frac{1}{r}\lambda\rho_{s'}^\circ d\mathbf{r}+\sum_{j\neq i}\int\frac{1}{r}A_j(\phi_j^\lambda-\phi_j^{(0)})d\mathbf{r}, \qquad \text{(A8)}$$

where s' is used to indicate that the first sum does not include a ρ_M°. Comparison with Eq. (1) shows that (A8) is the "ϕ_i" of a hypothetical system in which the charge distribution is $\lambda\rho_{s'}^\circ$ and in which ρ_M° vanishes. Inasmuch as the $\lambda(\phi_i-\phi_i^{(0)})$'s and the $(\phi_i^\lambda-\phi_i^{(0)})$'s can be shown to satisfy the same set of equations and the potential function is uniquely determined, Eq. (A9) then follows

$$\phi_i^\lambda-\phi_i^{(0)}=\lambda(\phi_i-\phi_i^{(0)}). \qquad \text{(A9)}$$

One also sees from (A8) that $\phi_i^\lambda-\phi_i^{(0)}$ is a linear functional of the $\lambda\rho_s^\circ$: It depends linearly on them and vanishes when all $\lambda\rho_s^\circ$ vanish. On introducing (A9) into (A7), equating the coefficients of λ^0, λ^1, λ^2 in (A7) to $U^{\text{pol}}(0)$, $U(1)$, and $U(2)$, and using (A10), Eqs. (A1) to (A3) are obtained

$$\sum_s\int\rho_s^\circ\phi_s^{(0)}d\mathbf{r}=\int\rho_M^\circ(\phi_M-\phi_M^{(0)})d\mathbf{r}. \qquad \text{(A10)}$$

To prove (A10) we note that $\phi_i^{(0)}$ is the "ϕ_i" of a system in which ρ_s° vanishes, and that $\phi_i-\phi_i^{(0)}$ is the "ϕ_i" of a system in which ρ_M° vanishes. Application of Eq. (39) of Ref. 7a then yields (A10).

To prove (A6) we note that $\eta_{i_{-0}}$ is the "ϕ_i" of a system in which ρ_M° vanishes and in which ρ_s° equals $\rho_{s_{-0}}^\circ$, while η_{i_1} is the "ϕ_i" of a system in which ρ_M° vanishes and in which ρ_s° is $\rho_{s_1}^\circ$. Application of Eq. (39) of Ref. 7(a) then yields (A6).

APPENDIX II: F VALUES FOR VARIOUS MODELS

1. Polarizable Point Dipole in a Sphere

The F value is given by

$$F=-\tfrac{1}{2}f^*\mu^2, \qquad \text{(A11)}$$

where f^* is given by (38).

2. Separated Pair of Charges in a Low-Dielectric-Constant Sphere

In this case the F value is given by[32]

$$F=-\tfrac{1}{2}c\mu^2, \qquad \text{(A12)}$$

where

$$c=A-\frac{D_i-D}{a^3D_iD}\sum_{n=0}^{\infty}\rho^n\left[1+\frac{D_i(n+\frac{1}{2})}{D(n+1)}\right]^{-1}, \qquad \text{(A13)}$$

where ρ equals $(r/a)^4$, $2r$ being the distance between the charges which lie along a diameter, equidistant from the center. In (A13) A is the same as the second term with D replaced by unity. The relation between D_i and α is given by Eq. (40b) (typically $D_i\cong D_{\text{op}}$). When the electronic polarization of the solute is ignored, D_i is set equal to unity.

When the $n=0$ term suffices in the two sums in (A13) (one sum is in A), the result reduces to (A11) when (40(b) is introduced for D_i.

3. Separated Pair of Charges in a Low-Dielectric-Constant Ellipsoid

When the charges are placed at the foci F is given by (A12), where now c is given by[33]

$$c=A-\frac{(D_i-D)\lambda_0^3}{a^3D_iD}\sum_{n=1,3,5\cdots}(2n+1)\times\left[\frac{P_n}{Q_n}-\frac{D_i}{D}\frac{dP_n/d\lambda}{dQ_n/d\lambda}\right]^{-1}. \qquad \text{(A14)}$$

In (A14) A is again the second term when D is replaced by unity, a is the semimajor axis of the ellipse, λ is a/r, $2r$ is the distance between the two foci, P_n and Q_n are Legendre functions (of λ) of the first and second kind. For large λ, the use of asymptotic expressions for P_n and Q_n leads readily to (A11).

In a calculation cited in the text, r/a was taken to be about $\frac{5}{6}$ for the substituted stilbenes, for the partial charges in the excited state were assumed to be centered on the electron-donating group and on the electron-accepting one. Comparison of this result for $h\Delta(\nu_a-\nu_f)$ with that for the $n=0$ term, i.e., with the dipolar term in (A13), indicates that the value of $\mu_e-\mu_g$ calculated from the shift is in error by 40% if only the dipolar term in (A13) is used. The percent error is, of course, less if the charge separation is less.

In the ion-pair calculation an effective polarizing radius a of 2.2 Å was used and a value of r/a of $\frac{1}{2}$ was assumed. Use of (A13) then shows that the $n=0$ term suffices. Kosower has suggested that the excited state, although not an ion pair, will have a dipole moment approximately normal to that of the former ion pair. In this case, the two charge distributions are

[32] Reference 24(a); derived from Eq. (6) there.
[33] Reference 24(b); derived from Eqs. (8), (13), and (15) there.

"orthogonal" in the sense defined earlier, and examination of Eq. (23) and (A11) shows that the usual shift should equal $f^*\mu_0^2$ plus a term independent of solvent polarity. From the slope of a plot of shift vs f^* the dipole moment μ_0 can be estimated. There is some uncertainty as to the value to be selected for α_0. A value of D_i of 2 in (40b) was used, although a better choice can undoubtedly be made. The dipole moment cited in the text is the "primary dipole" μ. The actual dipole moment is slightly different because of the solute's polarizability and the effect of the reaction field. The actual dipole can be computed from the primary one.

APPENDIX III: DERIVATION OF EQ. (46) FOR F

If the charge density on each ρ_s° is multiplied by λ and the corresponding ϕ_{sk} in system $[k]$ is denoted by ϕ_{sk}^λ, the value of F is given by the reversible work term

$$F=\int_{\lambda=0}^{\lambda=1}\int_{\mathbf{r}}\langle\phi_{sk}^\lambda\rangle_k^\lambda\rho_s^\circ d\mathbf{r}d\lambda, \tag{A15}$$

where $\langle\ \rangle_k^\lambda$ indicates an average with respect to the equilibrium distribution of configurations τ for the given λ. The statistical-mechanical equivalent of the dielectric unsaturation approximation is introduced by making $\langle\phi_{sk}^\lambda\rangle_k^\lambda$ linearly dependent on λ

$$\langle\phi_{sk}^\lambda\rangle_k^\lambda=\langle\phi_s^{(0)}\rangle+\lambda(\langle\phi_{sk}\rangle_k-\langle\phi_s^{(0)}\rangle), \tag{A16}$$

where $\langle\phi_{sk}\rangle_k$ and $\langle\phi_s^{(0)}\rangle$ are the equilibrium values of $\langle\phi_{sk}^\lambda\rangle_k^\lambda$ at $\lambda=1$ and $\lambda=0$, respectively.

Equations (A15) and (A16) then yield (46).

We conclude this Appendix by showing that (46) is the same as (4) but with the dielectric unsaturation approximation introduced. The proof is given, since it is the F defined by (4) which appears in Eqs. (13) and (30).

The averaging function appearing in $\langle\ \rangle_k$ is given by (9), (with the 0 replaced by k). We then use (7) for U, noting that $U(2)$ can be replaced by its average value since it is independent of ρ_M° and hence insensitive to changes of τ. On multiplying all ρ_s° by λ (and hence multiplying all linear functionals of ρ_s° by λ), expanding in a power series in λ and retaining only terms up to first order in λ (dielectric unsaturation approximation) we find

$$\langle\phi_{sk}\rangle_k=\langle\phi_{sk}\rangle-(1/kT)[\langle\phi_{sk}U_k(1)\rangle-\langle\phi_{sk}\rangle\langle U_k(1)\rangle], \tag{A17}$$

where $\langle\ \rangle$ denotes an average (9) but with U in the averaging function replaced by $U(0)$. From Eq. (46) we find (A18) with the aid of (A2) and (A3) and neglecting terms depending on the third power of the ρ_s°

$$F_k=\langle U_k(1)+U_k(2)\rangle-(1/2kT)[\langle U_k^2(1)\rangle-\langle U_k(1)\rangle^2]. \tag{A18}$$

However, this expression is precisely the one deduced elsewhere from Eq. (4) and used there to obtain (13) in the dielectric unsaturation approximation.[8a]